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13. ABSTRACT *(Maximum 200 words)*

The synthesis of multigram quantities of 1,3,3-trimethylcyclopropene was accomplished using a modified literature procedure. The stability of this material towards different conditions was studied. Oxygen reacts with the neat material to quickly form a thick polymeric gum which eventually solidifies to a white solid. In the presence of Lewis acids such as untreated glass or metals such as stainless steel or copper, neat cyclopropene will form a [2+2] dimeric product in high yield. Hydrocarbon solutions (e.g. RP-1) of the cyclopropene are much more stable to these mild Lewis acid conditions but will also produce the dimeric product. A multigram sample of the cyclopropene was sent for testing in the microthruster at Phillips Laboratory.

A convenient large scale synthesis of 3-chloro-2-chloromethylpropene was developed starting with pentaerythritol. This compound serves as the starting material for a two step synthesis of [1.1.1]propellane.

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Final Technical Report

SYNTHESIS OF POTENTIAL HIGH-ENERGY FUELS

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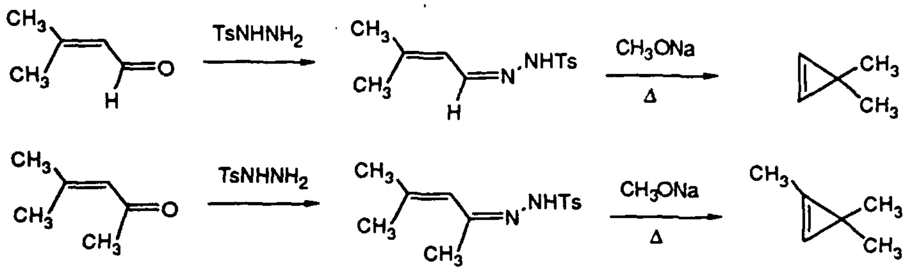
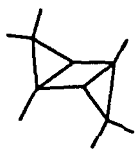
This final technical report covers work from June 1, 1992 to May 31, 1993 that was sponsored under F49620-92-J-0273 through the Air Force Office of Scientific Research. The objectives of this work were to 1) develop optimized procedures for the preparation of multigram quantities of 1,3,3-trimethylcyclopropene and 3,3-dimethylcyclopropene, and 2) investigate the kinetic stability and storability of these compounds. We have met these objectives. In addition, we have prepared quantities of 1,3,3-trimethylcyclopropene for testing by the Phillips Laboratory and have developed an improved procedure for the preparation of 3-chloro-2-chloromethylpropene.

On a per carbon basis, cyclopropene is one of the most energetic hydrocarbons that can be synthesized and manipulated. Cyclopropene itself has ΔH_f = 66 kcal/mol and a strain energy of 55 kcal/mol. The parent compound and substituted derivatives which have fewer than two substituents on the methylene carbon tend to be unstable. They undergo polymerization via an ene reaction. However, cyclopropenes that have two groups at the methylene carbon can be quite robust. For instance, 3,3-dimethylcyclopropene can be heated to 100 °C for extended periods without decomposition. We are investigating these compounds as potential high energy fuels and fuel additives.

We have synthesized 1,3,3-trimethylcyclopropene and 3,3-dimethylcyclopropene as shown below. The calculated Isp values for these compounds burned with liquid oxygen are 311 and 314 seconds respectively. The currently used hydrocarbon-based propulsion systems are based on RP-1 which has an Isp of 300 seconds. Thus these two fuels offer increases of greater than 4% over conventional fuels. The starting materials for the syntheses of these two compounds are all inexpensive, the reactions are easy to carry out and the major byproduct, p-toluenesulphonamide, can be recovered and transformed back into p-toluenesulphonylhydrazide.

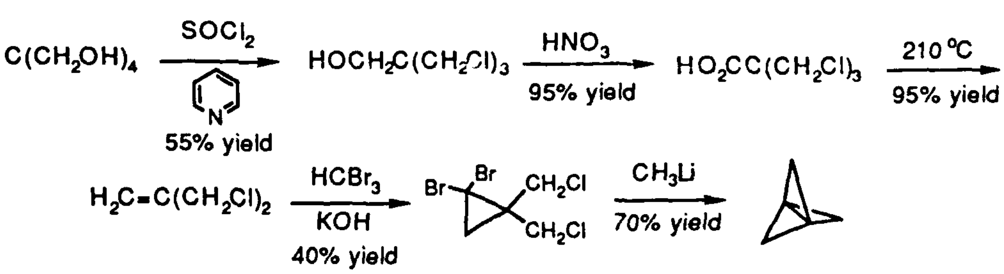


The stability of 1,3,3-trimethylcyclopropene was studied under several conditions. In the presence of oxygen, the compound turns to a thick gum and then to a white solid in the course of several days. This is presumably a polymer. If the compound is stored in a Pyrex container that has not been washed with base and EDTA solution, it will slowly form a dimeric product, a formally [2+2] product. This same material is formed in the presence of metals such as stainless steel or brass such as the fuel container for the microthruster at Phillips laboratory. This type of reaction has been reported for other cyclopropenes and is caused by Lewis acids. If the cyclopropene is diluted with a solvent such as RP-1 it reacts much more slowly and can be left in the container for many hours without significant dimerization. We believe that the structure is the following.



A 50 gram quantity of 1,3,3-trimethylcyclopropene was sent to the Phillips Laboratory for testing in their microthruster.

Another class of strained-ring compounds that are of interest as high energy fuels is based on the bicyclo[1.1.1]pentane system. This is a highly strained (SE=66 kcal/mol) system but is kinetically extremely stable. The parent bicyclo[1.1.1]pentane is a structural isomer of the dimethylcyclopropenes and has the same enthalpy of formation but exhibits much greater stability. The most direct entry into this ring system is based on the chemistry of [1.1.1]propellane. [1.1.1]propellane is conveniently prepared in two steps starting with 3-chloro-2-chloromethylpropene. Unfortunately, this material is reasonably expensive and the published literature routes are low yielding and/or dangerous. We have recently developed a convenient and economical synthesis of this compound starting with pentaerythritol ($10/kg).



All of these reactions can be carried out on a very large scale and the products are easy to purify. We are in the process of submitting this procedure to Organic Syntheses.

[1.1.1]Propellane is a highly energetic molecule that can be converted into other useful high energy materials. Some of these compounds along with their predicted Isp values are shown below.

I_{sp}	316.6	313.9 sec	311.2	309.9

Our future efforts will be directed at efficient syntheses of several of these compounds for testing at the Phillips Laboratory.

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